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Extraction, identification and adsorption-kinetic studies of a natural color component from *G. sepium*

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ABSTRACT

The use of synthetic dyes causes environmental pollution as majority of these dyes are toxic and non-biodegradable. Natural dyes on the other hand have proved to be eco-friendly, biodegradable and highly compatible with the environment. Consequently, dyes derived from natural sources have emerged as important alternatives to synthetic dyes. In the present work, the major color component isolated from the pods of *G. sepium* plant is morin, which is a flavonoid moiety. The dyeing behaviour of this component on silk yarn was investigated. Mordanting studies have indicated that the post-mordanting method was found to be a better method compared to pre-mordanting. Variation of pH on dye extract pointed out that the maximum absorbance was at pH 4 and hence all the dyeing studies have been carried out at that pH. Thermodynamic parameters were determined by studying the dyeing process at different temperatures. Heat of dyeing was positive which indicated the dyeing process was endothermic. The adsorption process of morin on silk was tested with Langmuir, Freundlich and Tempkin-Pyzhev isotherm models. The adsorption process followed both the Langmuir and Freundlich isotherms. The value of regression coefficient, however, indicated that the Langmuir isotherm was a better fit than the Freundlich isotherm. These results signified that the adsorption of morin on silk yarn was homogeneous in nature with the formation of a monolayer. Hence, the dye obtained from the pods of *G. sepium* plant may be an alternative source to synthetic dye for the dyeing of silk as well as other textile fabrics.

Keywords: G. Sepium; Morin; Adsorption-Kinetics; Silk

1. INTRODUCTION

The use of synthetic dyes causes environmental pollution as majority of these dyes are toxic and non-biodegradable. For this reason, there is a revival of interest in the non-toxic and eco-friendly natural dyes. Nature provides a wealth of plants which yield color for the purpose of dyeing, many have been used since antiquity [1-4]. Natural dyes exhibit better biodegradability compared to their synthetic counterparts and generally have a higher compatibility with the environment. There are several reports in the literature pertaining to the application of natural colorants and evaluation of their dyeing properties on various fibers [5-8], but a very few reports are available on their kinetic and adsorption aspects [9-11]. *G. sepium*, is an important member of the family Fabaceae, which is widely naturalized in the tropical Americas, Caribbean, Africa, Asia, and the Pacific Islands. Since this tree possesses high nitrogen-fixing properties and also the leaves can be used for mulch and green manure, which makes it highly suitable in agro-forestry systems. *G. sepium* is a small, thornless, semi-deciduous tree, which yields flattened pods, 10-15 cm long, containing three to eight seeds. The abundantly available pods, unless otherwise used go as natural waste.

Keeping this in view and also due to our continued interest in the identification of colorant from natural plants, a major color component from the pods of *G. sepium* plant was identified. The present research was performed with the following objectives: 1) To extract and isolate the main color component from the pods of *G. sepium* plant, 2) To explore the dyeing properties of the color component on silk, 3) To study adsorption isotherms of the color component on silk and 4) To evaluate the thermodynamic parameters of the dyeing process through kinetic studies.

2. MATERIALS AND METHODS

2.1. Materials

The pods of *G. Sepium* were collected from the south-eastern region, Shimoga, India. The pods were washed well with tap water and dried under laboratory conditions. The dried pods were then finely ground to powder. Raw silk yarn of 40 denier was scoured with 2 g dm^{-3} non-ionic detergent and 1 g dm^{-3} sodium carbonate at 90℃ for 1 h, and rinsed with water and dried under laboratory conditions.

2.2. Isolation

The air dried powder of *G. Sepium* pod (550 g) was extracted with 90% methanol (3 × 250 ml) at room temperature using a soxhlet apparatus and the procedure was repeated till the color from the extract was negligible. The extracts were combined, concentrated under reduced pressure and the residue was successively extracted with pet. ether, chloroform and ethyl acetate. The ethyl acetate soluble fraction was concentrated under reduced pressure and was chromatographically separated over silica gel (60-120 mesh) using methanol as eluent. The fractions obtained were combined according to TLC (silica gel, $CHCl_3$-MeOH-H_2O, 80:18:2) in increasing order of polarity to yield two fractions. Solvent was evaporated from the first fraction (major) to get yellow colored amorphous compound and it was used for further studies.

2.3. Mordanting

Pre-and post-mordantings were carried out on silk using 2, 4 and 6% tannic acid and alum ($Al(NH_4)(SO_4)_2.12H_2O$) as mordants, separately. Mordanting was carried out for 30 min at 70℃ and the silk was then rinsed with tap water and dried.

2.4. Dyeing

Open bath beaker dyeing machine equipped with programmable control of temperature and time was used to carry out all dyeing studies. The silk yarn was dyed with 4% dye solution at pH 4 with M: L ratio of 1 : 20. The dyeing was started at 40℃ and the temperature was gradually raised to 90℃ in 20 min and the dyeing process was continued for 45 min. After dyeing, samples were removed from dyeing machine and soaped at 60℃ for 10 min. Further, the samples were rinsed with tap water and dried. In case of post-mordanting samples, soaping was done after mordanting.

2.5. Characterization

IR spectrum of the major color component was recorded on a Perkin-Elmer 298 grating IR Spectrophotometer. The NMR spectrum of the compound was recorded on the Brucker 400 NMR spectrophotometer. The mass spectrum was recorded on an Esquire 3000 plus spectrometer.

2.6. Absorbance and Color Strength Measurements

The dye solutions (1-5%) of the extract were prepared with M: L ratio of 1 : 20. The absorbance of the dye solutions was recorded prior and after the dyeing process using UV-Vis spectrophotometer. The dye exhaustion was calculated using the equation, % Exhaustion = $[(C_g-C_t)/C_g] \times 100$, where C_g is the concentration of dye offered and C_t is the concentration of residual dye in the spent liquor.

The surface reflectance and colorimetric data (CIE L^* a^* b^* C h) for the dyed samples were obtained by Gretag Macbath Color Eye 7000A spectrophotometer. The spectrophotometer was interfaced to a PC under illuminant D_{65} with a 10^0 standard observer. Surface color strength (K/S) was calculated from the surface reflectance values using the Kubelka-Munk equation [12]: $K/S = (1-R)^2/2R$, where R is the reflectance, K is the absorption coefficient and S is the light scattering coefficient. A higher K/S value signifies better dye receptivity of the substrates. The wash fastness of the dyeing was tested using ISO method 105-C10-A(1)-2006 and crocking fastness was assessed using AATCC Test Method 8-1996. Color fastness to light was evaluated as per AATCC Test Method 16-2004 option 5.

2.7. Kinetic Studies

Kinetic studies were investigated with aqueous solution of the dye extract 0.5 g dm^{-3} (without any further purification) prepared in an acetate buffer of pH 4. The dyeing was carried out with M:L ratio of 1:20 at 50℃. Known volume (5 ml each) of the dye-bath solution was pipetted into a cuvette at regular intervals of time and absorbance measurements were made at its λ_{max} 580 nm (**Figure 1**). The absorbance readings of D_o and D_t at the beginning and at any time interval during the dyeing process,

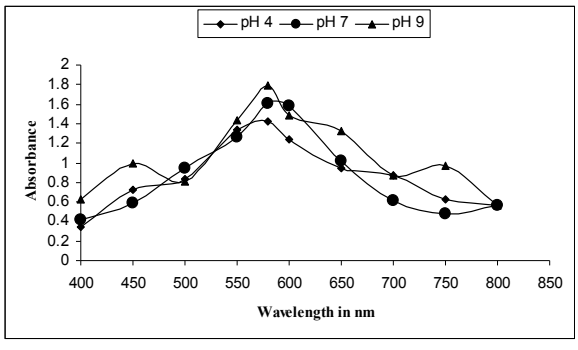

Figure 1. Visible Spectra of *G. sepium* in aqueous solution at different pH.

respectively, were recorded. Plots of log (D_o/D_t) versus time were made to evaluate first-order rate constants (k/s^{-1}). The experiment was repeated at 60, 70 and 80^{0}C and the dye uptake rate was calculated at each temperature. The energy of activation and other thermodynamic parameters were deduced.

2.8. Adsorption Isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the adsorbate and adsorbent when the adsorption process reaches an equilibrium state. The amount of dye adsorbed at equilibrium q_e (mg/g) was calculated by the following mass balance equation [13]:

$$q_e = V(C_i - C_e)/M \quad (1)$$

where V is the volume of solution used in the adsorption experiment, C_i and C_e are the initial and equilibrium concentrations of the dye (mg dm^{-3}), respectively, and M is the mass of silk (g).

In the present case, the adsorption isotherm study was carried out on Langmuir, Freundlich and Tempkin-pyzhev isotherms. The applicability of the isotherm equation was compared by judging the value of regression coefficients (r). The equilibrium adsorption isotherm is fundamental in describing the interaction between adsorbent and adsorbate, and is also important in the design of an adsorption system. A basic assumption of Langmuir theory is that in which the sorption takes place at specific homogeneous sites within the adsorbent. It is then also assumed that once a dye molecule occupies a site, no further adsorption can take place at that site. Theoretically, a saturation value is reached beyond which no further sorption can take place. The Langmuir isotherm [14] was applied for adsorption equilibrium and represented as:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

where C_e = Concentration of adsorbent (mg dm^{-3}) at equilibrium; q_e = Amount of dye adsorbed at equilibrium (mg/g); $Q_o = A$ constant (mg/g) which signifies the practical limiting adsorption capacity when the surface is fully covered with dye molecules and it aids in the comparison of adsorption performance and b = Langmuir constant related to the affinity of the binding sites (cm^{-3} mg).

Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage. The well known logarithmic form of Freundlich model [15] is given by the following equation:

$$\log q_e = \log K_f + \frac{\log C_e}{n} \quad (3)$$

where K_f and $1/n$ = Freundlich constant related to adsorption capacity and adsorption intensity respectively obtained from the plot. In general, as the K_f value increases the adsorption capacity of the adsorbent for the given adsorbate increases. $1/n$ is the heterogeneity factor, if n is close to unity, the surface heterogeneity could be assumed to be less significant and as n approaches 10, the impact of surface heterogeneity becomes more significant [16].

Tempkin and Pyzhev [17] considered the effects of indirect adsorbate-adsorbent interactions on the adsorption isotherms. As a result, the heat of adsorption of all the molecules on the adsorbent surface layer would decrease linearly. The Tempkin isotherm can be expressed in its linear form as:

$$q_e = B \ln A + B \ln C_e \quad (4)$$

where B and A are the Tempkin constants and can be determined by a plot of q_e versus ln C_e. The constant B is related to heats of adsorption and A is the equilibrium binding constant.

3. RESULTS AND DISCUSSION

3.1. Characterization of Major Color Component

Morin (2', 3, 4', 5, 7-Pentahydroxyflavone) [18-20] was isolated from the pods of *G. sepium* as the major color component and it was confirmed by IR, ^{1}H-NMR, ^{13}C-NMR and Mass spectral studies.

3.2. Effect of Dye Concentration and Color Strength

Table 1 revealed that the absorption of dye increased with increase in dye concentration (1-5%) and the maximum dye uptake was observed at 4% concentration. The values of K/S also increased with the increase in dye concentration (**Table 1**). Further, it was noticed that the K/S value was higher at 4% dye concentration, indicating deeper shades at higher concentrations. Therefore, 4% dye concentration was fixed as optimal concentration for further dyeing process.

Table 1. Absorbance (%) and K/S values of different dye concentrations at 360 nm.

Dye oncentration (%)	Absorbance		Dye uptake (%)	K/S
	Before dyeing	after dyeing		
1	0.13	0.10	23.0	4.14
2	0.27	0.19	29.6	4.28
3	0.47	0.31	34.0	4.43
4	0.61	0.33	45.9	4.50
5	0.84	0.55	34.5	4.45

3.3. Effect of Mordanting

The K/S values of the mordanted samples were better compared to that of the un-mordanted samples (**Table 2**). The K/S values and the fastness properties (**Table 3**) of the post-mordanted samples were better compared to pre-mordant samples. Tannic acid was found to be a better mordant with deeper shades and fastness ratings as compared to alum in pre-mordanting. But in case of post-mordanting, both the mordants showed comparable K/S values. All the color co-ordinates were positive and hence the dyed samples were located in the yellow-red quadrant of the color-space diagram.

3.4. Effect of pH on Dye Extract

The visible spectrum of the dye extract at different pH (4, 7 and 9) is illustrated in **Figure 1**. The λ_{max} of the dye extract remained the same with varying pH. The absorbance of the dye extract increased with an increase in pH, which may be due to the high solubility of phenolic groups in the alkaline pH.

3.5. Kinetic Studies

From the linear plot log $k^{/}$ versus 1/T (r = 0.9979), the energy of activation (E_a) was found to be 61.2 kJ mol^{-1}. Further, thermodynamic parameters such as $\Delta H^{\neq}$, $\Delta G^{\neq}$,

Table 2. Color co-ordinates and K/S values of the dyed silk samples.

Method	Mordants	K/S	L^*	a^*	b^*	C	h
Pre	Nil	4.50	63.1	15.1	17.3	23.0	48.9
	Alum (2%)	4.61	69.7	11.5	14.1	18.2	50.5
	Alum (4%)	4.63	69.7	11.7	13.8	18.1	49.5
	Alum (6%)	4.73	69.9	11.8	13.9	18.2	49.6
	Tannic acid (2%)	5.22	75.2	9.85	12.0	15.5	50.7
	Tannic acid (4%)	5.27	74.3	10.1	12.8	16.3	51.6
	Tannic acid (6%)	5.37	74.9	9.41	12.7	15.8	53.5
Post	Alum (2%)	5.76	62.5	12.9	23.5	26.9	61.1
	Alum (4%)	5.55	63.1	13.2	22.8	26.3	59.9
	Alum (6%)	5.44	62.8	13.2	22.9	26.5	60.1
	Tannic acid (2%)	5.66	68.1	12.7	17.4	21.6	53.7
	Tannic acid (4%)	5.57	68.7	12.4	17.5	21.5	54.5
	Tannic acid (6%)	5.30	66.2	13.2	19.9	23.9	56.3

L^*- Lightness, a^* - (+ ve- red, - ve- blue), b^* - (+ ve- yellow, - ve- green), C-Chroma and h-Hue.

Table 3. Results derived from fastness properties of dyed silk samples.

	Mordants	light fastness	crocking fastness		wash fastness
			wet	dry	
Pre	Nil	2	4	4-5	3-4
	Alum (2%)	2	4-5	4-5	4
	Alum (4%)	2-3	4-5	5	4-5
	Alum (6%)	2-3	4-5	5	5
	Tannic acid (2%)	2-3	4-5	5	4-5
	Tannic acid (4%)	2-3	5	5	5
	Tannic acid (6%)	3	5	5	5
Post	Alum (2%)	2	4-5	4-5	4
	Alum (4%)	2	4-5	4-5	4
	Alum (6%)	2-3	4-5	5	4-5
	Tannic acid (2%)	2	4-5	4-5	4
	Tannic acid (4%)	2-3	5	5	4-5
	Tannic acid (6%)	2-3	5	5	5

$\Delta S^{\neq}$ and log A were calculated and recorded in **Table 4**. The high positive value of the standard free energy ($\Delta G^{\neq}$) indicates the spontaneous and strong adsorption of dye molecules on the surface of silk. The enthalpy of dyeing or heat of dyeing ($\Delta H^{\neq}$) was positive indicating that the dyeing process is endothermic in nature. Further, large negative entropy ($\Delta S^{\neq}$) indicates that the dye molecules are more systematically arranged on the surface of silk yarn.

3.6. Adsorption Isotherms

The experimental adsorption data were analyzed using Langmuir, Freundlich and Tempkin and Pyzhev isotherm models. The Langmuir constants Q_o and b were deduced from the intercept and slope of the plot $1/q_e$ versus $1/C_e$. The plot was linear with a regression value of r = 0.9987 (**Figure 2**). The value of Q_o was found to be 142 mg/g, signifies the amount of dye required to form a complete mono layer at equilibrium. The value of Langmuir constant b = 1.97 cm^3/mg, which relates with the binding energy of dye molecules on silk. Further, the essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor for equilibrium parameter, R_L [21-23]:

$$R_L = \frac{1}{(1+bC_o)} \quad (5)$$

where C_o is the initial concentration of dye (mg/dm^3) and b is the Langmuir constant (mL/mg). The value of R_L indicates the type of isotherm to be either irreversible (R_L= 0), favorable (0 < R_L< 1), linear (R_L = 1) or unfavorable (R_L > 1). In the present study, the value of R_L was found to be 0.835, indicating that Langmiur adsorption isotherm to be a favorable process.

A plot of log q_e versus log C_e was a straight line with a regression coefficient of 0.9975 (**Figure 3**) for Freundlich adsorption isotherm. The values of K_f and $1/n$, were calculated from the intercept and slope of such a plot and were found to be 2.50 and 0.84, respectively. The value of $1/n$ indicates that the adsorption process is homogeneous, as the value is very close to unity.

Further, Tempkin and pyzhev model was also considered to correlate the experimental data. The plot of q_e versus log C_e was curvilinear with regression coefficient r = 0.9560 (**Figure 4**).

The linear regression coefficient was normally used to decide the most fitted isotherm in adsorption process. As seen from **Table 5**, the Langmuir model yielded somewhat better fit (r = 0.9987) than the other models fitted. The results demonstrated the formation of homogeneous monolayer. Further, the value of $1/n$ (0.84) in Freundlich isotherm model also supports the formation of monolayer.

4. CONCLUSIONS

The major coloring component obtained from the pods of the *G. sepium* was identified as morin, a flavonoid. The dyeing behaviour of this component on silk yarn was investigated. Mordanting studies have indicated that the post-mordanting method was found to be a better method compared to pre-mordanting. For dyeing of silk, heat of dyeing ($\Delta H^{\neq}$) was positive which indicates endothermic nature of the process. The negative value of $\Delta S^{\neq}$ indicates a more ordered adsorption of color component on silk. The high positive value of free energy change signifies that the color component has stronger affinity

Table 4. Kinetic and thermodynamic parameters for the dyeing of coloring matter on to silk yarn.

Temperature (^{0}C)	10^4 k/ (s^{-1})
50	2.64
60	4.79
70	9.25
80	18.4
E_a (kJ mol^{-1})	61.2
$\Delta H^{\neq}$ (kJ mol^{-1})	58.4
$\Delta G^{\neq}$ (kJ mol^{-1})	103
$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	-133
log *A*	6.32

Table 5. Isotherm constants for silk dyeing with pods of *G. sepium* extract.

Langmuir isotherm constants	
Q_o (mg/g)	142
b (mL/mg)	1.97
r	0.9987
Freundlich isotherm constants	
K_f (mg/g)	2.50
$1/n$	0.843
r	0.9975
Tempkin and Pyzhev isotherm constants	
B (mg/g)	3.43
A (mL/mg)	1.46
r	0.9560

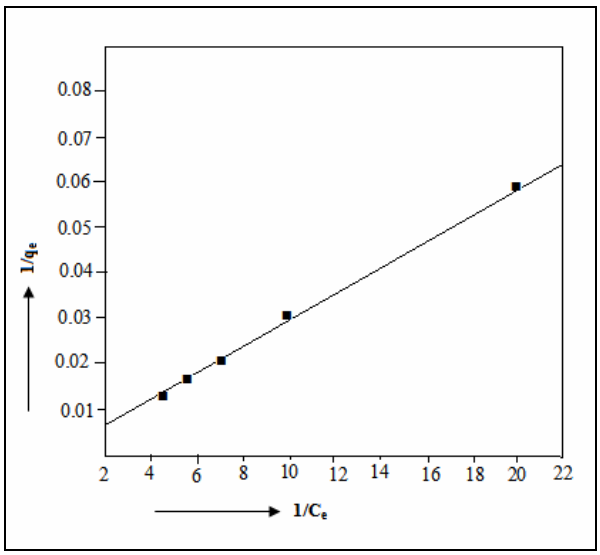

Figure 2. Langmiur isotherm plot at pH 4 for dyeing silk with color component of *G. sepium* at 80℃.

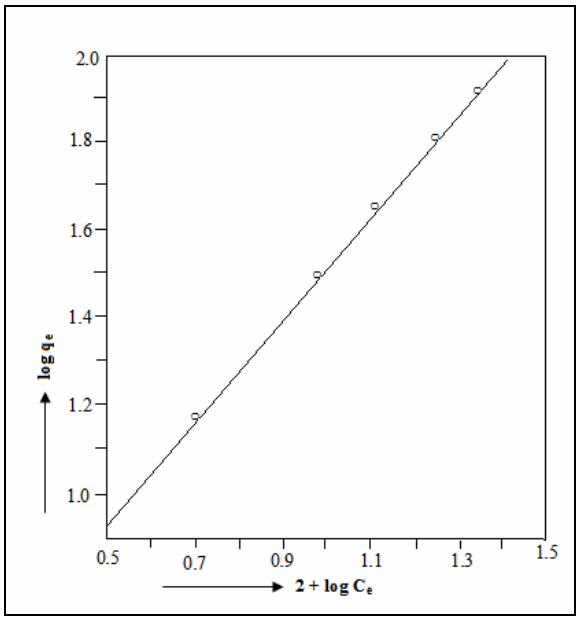

Figure 3. Freundlich isotherm plot at pH 4 for dyeing silk with color component of *G. sepium* at 80℃.

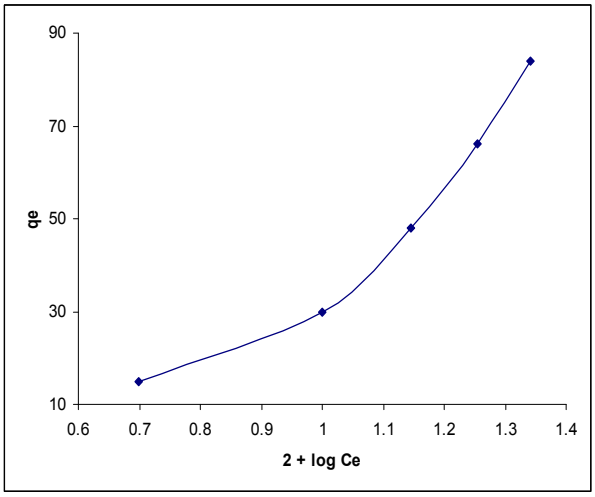

Figure 4. Tempkin and Pyzhev isotherm plot at pH 4 for dyeing silk with color component of *G. sepium* at 80℃.

towards silk. The adsorption isotherm of morin on silk was carried out using different models: Langmuir, Freundlich and Tempkin-Pyzhev models. The adsorption of morin on silk fitted well to the Langmuir and Freundlich isotherm. However, Langmuir model was found to be better fit, and suggesting the formation of homogeneous monolayer on silk.

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